METHOD OF REFORMING ELEMENT SURFACE, ELEMENT WITH REFORMED SURFACE, METHOD OF MANUFACTURING ELEMENT WITH REFORMED SURFACE, SURFACE TREATMENT LIQUID FOR FORMING REFORMED SURFACE, AND METHOD OF MANUFACTURING SURFACE TREATMENT LIQUID

Background of the invention

Field of the invention

The present invention relates to a method of reforming surface of an element for changing characteristics, properties, or the likes to provide desired characteristics and properties, which is applied to the surface of an element (the inner face, outer face, or both of the element) or the surface of an element whose surface has been subjected to some treatment and the present invention also relates to any element subjected to the surface reforming treatment.

The present invention especially relates to a surface reforming method which can be carried out to reliably reform the surface of an element such as a fiber, a particle, or a container made of an olefinic resin difficult to be surface-treated but harmless to environments and relates to a method of manufacturing an element and a fiber having reformed surface.

Related Background Art

Conventionally, though the characteristics and the properties of an element are dominated with the

characteristics of the constituent material, a desired characteristic is provided by reforming the surface characteristic. The desired characteristic sometimes means a reactive group having a reactive property such as water-repelling property and hydrophilicity or a reactive group reactive to an adduct or the like.

In general, such a conventional surface reforming is carried out by making the surface radical using ozone or UV or ozone in combination with UV and forming chemical bond of a main component of a treatment agent with the surface. On the other hand, a desired characteristic is obtained for a moment by sticking a treatment agent having the very desired characteristic itself to the element surface without making the surface radical and in this case, the continuity is usually lacking. Especially, regarding the hydrophilicity for an olefinic resin harmless to environments, it is only known that incomplete hydrophilic condition, which is insufficient in the continuity for a long duration, can temporarily be provided by mixing a surfactant with a treatment agent for producing hydrophilicity in the presence of a liquid.

On the other hand, an adhesive or a primer is conventionally used to form an additive layer on an element. Regarding them, in order to use a primer such as a silane coupling agent which is bonded to the

surface of an element only by the chemical reaction, the element has to be treated to be reactive.

As another type primer, those which are of similar materials to that of an element are available to utilize the affinity to the element. As such a primer, an acid-deformed polypropylene chloride is known which is used at the time when an upper coating layer of a polyurethane resin is formed on polypropylene. However, in the case where a primer of a similar material to that of the surface of an element, the element is consequently increased in the volume and additionally requires a technique to form a thin and uniform coating. Also, the primer can not be supplied evenly to a fine element or to the inner parts of a porous body. Especially, the acid-deformed polypropylene chloride can not be used in an aqueous solution state as it is insoluble in water, the way of using it is limited.

As a result, no material has been available which is soluble in water to be an aqueous solution and can be applicable to form a thin and uniform surface reforming layer regardless of the shape of the element even among materials different from that of the surface of an element.

To describe the present invention in relation to the background of the related arts in the relevant field, the present invention is innovative and achieved

being based on new findings found by examining the conventional technical standards.

The surface reforming only based on the chemical bonding by radicalizing the surface in a conventional manner is valid to treat an extremely narrow plane but often invalid to carry out sufficient and even surface reforming of the whole spherical surface, the inner or outer surface of a tube. Further, it is especially difficult to carry out the surface reforming treatment for the inside of an element comprising a complicated porous part such as a sponge and fibrous composite body and void parts among fibers.

In addition to that, in the case where a surfactant or the like is added to a liquid, the surface reforming of an element is not actually carried out and the characteristic is lost at the time when the surfactant is eliminated and the original characteristic of the surface itself is instantaneously appears.

Moreover, though an olefinic resin has excellent in water-repelling property meaning that the contact angle to water is 80 degree or higher and is utilized in almost all fields and applicable to a considerably wide range of use purposes, the surface reforming method is scarcely available as to provide a desired characteristic durable for a long duration.

The present inventors have examined as to provide

a method for reforming surface of any element by rationally carrying out surface reforming, at first, of an olefinic resin and explicating a method for maintaining the reformed characteristic and focused upon the use of a liquid phase treatment solution presupposing that the surface treatment is possible even to an element with a complicated shape.

As new findings of inventors of the present invention, the inventors have found that the balance between functional groups (e.g. hydrophilic groups) and the surface of an element to be treated is well controlled to be a desired state by utilizing the surface energy in a relation between the surface to be treated and a polymer having the functional groups (e.g. hydrophilic groups) and that the durability of the reformed surface and the stability of the quality can further be heightened by analyzing the polymer itself.

SUMMARY OF THE INVENTION

The following is the description of the technological objects to be solved by the present invention. The present invention is neither to process an element in the above described manner of radicalizing the characteristic of an element with ozone or UV rays nor to form a primer coating of such as a silane coupling agent, which sometimes causes

coating unevenness but aims mainly to provide an innovative surface reforming method capable of carrying out a desired surface reforming based on a new mechanism and a treatment solution to be used for the method, to provide an element obtained by the method, and to provide the surface structure itself obtained by the surface treatment.

A first purpose of the present invention is to provide a liquid-phase treatment solution capable of carrying out a desired surface treatment to a whole inner surface of an element having a complicated shape, such as a porous body and a finely processed element, and a surface reforming method using the treatment solution.

A second purpose of the present invention is to provide a new surface reforming method capable of maintaining the reformed characteristic for a long duration as compared with a conventional method for an olefinic resin, which has been supposed to be difficult to be treated for surface reforming, and to provide a surface structure itself.

A third purpose of the present invention is to provide a new surface reforming method capable of forming a thin layer of a thickness in a molecular level, preferably a monomolecular level, as a reformed surface itself without changing a structure of an element or with scarcely increasing the weight of the

element and to provide a surface structure itself.

A fourth purpose of the present invention is to provide a treatment method with which a desired reforming can freely be carried out by introducing a new mechanism into a surface reforming method itself.

A fifth purpose of the present invention is to provide a method for easily manufacturing a surface-reformed element with high productivity.

A sixth purpose of the present invention is to provide an innovative method for reforming element surface utilizing interfacial physical adsorption based on an energy level approximately similar to cleaving of a polymer from the view point of interfacial energy of a group (or groups) of the polymer.

A seventh purpose of the present invention is to provide an innovative surface reforming method capable of evenly reforming a circumference of an element and at the same time to provide a surface structure which has not been obtained by a conventional manner from the view point of the whole circumference of the surface structure itself.

Other purposes of the present invention may be understood from the following descriptions, and the present invention can achieve compounded purposes in an optional combination of the above described respective purposes.

The following inventions are included in the

present invention in order to achieve the above described purposes.

One aspect of a surface reforming method of the present invention is a surface reforming method for reforming a part of surface by providing a partial surface, which composes at least a part of the surface of a prescribed element, to be subjected to surface reforming with a functional group for surface reforming and is characterized in that the above described supply of the functional group to the above described partial surface is carried by a method involving a first step of supplying, to the above described partial surface, a liquid containing a polymer which is different from a constituent material of the partial surface and which composes a first part having the functional group and a second part having a group with an interfacial energy of approximately equal to the surface energy of the partial surface but different from the interfacial energy of the forgoing functional group and a second step of orienting the second part of the above described polymer toward the above described partial surface and orienting the first part toward the different side from the above described partial surface.

Another aspect of a surface reforming method according to the present invention is a surface reforming method for reforming a part of the surface by

providing a partial surface, which composes at least a part of the surface of a prescribed element, to be subjected to the surface reforming with a functional group for surface reforming and is characterized in that the above described supply of the functional group to the above described partial surface is carried by a method involving a first step of supplying, to the above described partial surface, a liquid containing fractionalized (dragmented) products which are obtained by cleaving of a polymer composing a first part having the above described functional group and a second part having a group with an interfacial energy of approximately equal to the surface energy of the partial surface but different from the interfacial energy of the forgoing functional group and which contain the above described first part and the above described second part, a second step of orienting the second part of the above described fractionalized products toward the above described partial surface and orienting the first part toward the different side from the above described partial surface, and a third step of at least partially polymerizing the fractionalized products oriented on the above described partial surface by condensation polymerization.

One aspect of an element having the surface reformed by a method of the present invention is an element provided with a polymer compound in a partial

surface composing at least a part of the surface and is characterized in that the above described polymer compound is a material which is either soluble in a solvent or has a main skeleton different from the material at least partially composing the forgoing partial surface and which comprises a first part having a functional group for reforming the above described partial surface and a second part having the interfacial energy different from the interfacial energy of the above described functional group and approximately equal to the surface energy of the above described partial surface and the above described second part is oriented toward the above described partial surface and the above described first part is oriented in the direction different from that of the above described partial surface.

Another aspect of an element having the surface reformed by a method of the present invention is an element provided with a polymer compound in a face made of a polymer material having 80° or wider contact angle to water and is characterized in that the above described polymer compound is a material which is either soluble in a solvent or having a main skeletal structure different from the above described polymer material and which comprises a first part having a hydrophilic group and a second part having the interfacial energy lower than the interfacial energy of

the above described hydrophilic group and approximately equal to the surface energy of the above described face made of the polymer material and the above described second part is oriented toward the face made of the above described polymer material and the above described first part is oriented in the direction different from that of the face made of the above described polymer material to give hydrophilicity to the face made of the above described polymer material.

A fibrous body with reformed surface formed by the present invention is a fibrous body made of a fiber, having an olefinic resin at least in the surface and provided with a polymer compound in the above described surface and is characterized in that the above described polymer compound is a material which is either soluble in a solvent or having a main skeletal structure different from the above described material forming the surface and which is a polyalkylsiloxane comprising a hydrophilic group and the alkyl group of the polyalkylsiloxane is oriented toward the above described surface and the above described hydrophilic group is oriented toward the direction different from the above described surface side to provide the above described surface with hydrophilicity.

One aspect of a method for manufacturing a fiber with reformed surface by the present invention is a method of manufacturing a fiber having an olefinic

resin at least in the surface and provided with a reformed surface having hydrophilicity in the above described surface and is characterized by comprising a first step of supplying a solution containing a dissolved alkylsiloxane polymer having a hydrophilic group to the above described surface and a second step of orienting the above described alkylsiloxane to the above described surface and orienting the above described hydrophilic group in the different direction from the above described surface.

Another aspect of a method of manufacturing a fiber with reformed surface by the present invention is a method of manufacturing a fiber having an olefinic resin at least in the surface and provided with a reformed surface having hydrophilicity in the above described surface and is characterized by comprising a first step of supplying to the above described surface a solution containing dissolved fractionalized products obtained by cleaving of an alkylsiloxane polymer having a hydrophilic group and a second step of condensing the above described fractionalized products on the above described surface, orienting the above described alkylsiloxane to the above described surface and orienting the above described hydrophilic group in the different direction from the above described surface.

Another aspect of a method of manufacturing a fiber with reformed surface by the present invention is

a method of manufacturing a fiber having an olefinic resin at least in the surface and provided with a reformed surface having hydrophilicity in the above described surface and is characterized by comprising a step of forming a fiber surface coated with a treatment solution containing a polyalkylsiloxane having a hydrophilic group, an acid, and an alcohol and a step of drying the treatment solution coating the above described fiber surface at a temperature higher than a room temperature.

Another aspect of a method of manufacturing a fiber with reformed surface by the present invention is a method of manufacturing a fiber having an olefinic resin at least in the surface and provided with a reformed surface having hydrophilicity in the above described surface and is characterized by comprising a step of forming a fiber surface coated with a treatment solution containing a polyalkylsiloxane having a hydrophilic group, an acid, an alcohol, and water and a step of drying the treatment solution coating the above described fiber surface while making the above described surface hydrophilic by orienting the above described hydrophilic group in the opposed direction to the above described surface.

Another aspect of a surface reforming method according to the present invention is a surface reforming method of the surface of a prescribed element

and is characterized by comprising a first step of supplying, to the above described surface, a liquid containing a diluted sulfuric acid, a volatile agent for reforming the affinity with the element surface and a treatment agent of a polymer comprising a second part having a group with an interfacial energy approximately equal to the surface energy of the above described surface and a first part having a group with an interfacial energy different from the above described interfacial energy, a second step of removing the above described agent for reforming the affinity by heating the resultant surface, a third step of cleaving the polymer in the above described treatment agent by concentrating the above described diluted sulfuric acid to a concentrated sulfuric acid, and a fourth step of condensing the ring-opened polymer on the above described surface and at the same time orienting the second part of the polymer toward the above described surface and orienting the first part in the different side from the above described surface.

Another aspect of a surface reforming method according to the present invention is a method for reforming the surface of an element by introducing a functional group to the forgoing surface and is characterized by involving a step of condensing fractionalized products comprising a second part having a group with an interfacial energy approximately equal

to the surface energy of the above described surface and a first part having the above described functional group and obtained by cleaving a polymer compound having the above described first part and the above described second part in the condition wherein the fractionalized products are oriented based on the affinity of the group having the interfacial energy approximately equal to the surface energy with the above described surface.

Another aspect of an element having a reformed surface by the present invention is an element having a reformed surface into which a functional group is introduced and is characterized by bearing a condensate substance of fractionalized products in the above described surface: and the above described fractionalized products comprise a second part having a group with an interfacial energy approximately equal to the surface energy of the above described surface and a first part having the above described functional group are obtained by cleaving a polymer compound having the above described first part and the above described second part, and are condensed in the condition wherein the fractionalized products are oriented based on the affinity of the group having the interfacial energy approximately equal to the surface energy with the above described surface.

Another aspect of an element having a reformed

surface by the present invention is an element having a circumferential part of a curved face forming a closed circular shape as an outer circumferential cross-section and is characterized in that the above described outer circumferential part has a part coated with a film containing a polymer and circularly surrounded with the film in one closed turn as to reform the forgoing surface part; and the above described polymer compound is a material which is soluble in a solvent or has a main skeletal structure different from the material of the surface of the element and which comprises a first part having a functional group for reforming the above described surface and a second part having the interfacial energy different from that of the above described functional group and approximately equal to the surface energy of the above described surface and the above described second part is oriented toward the above described surface and the above described first part is oriented in the direction different from that of the above described surface.

Another aspect of a surface reforming method of the present invention is a surface reforming method for reforming the hydrophobic surface of an element to be hydrophilic and is characterized by involving a step of sticking, to the above described hydrophobic surface, fractionalized products comprising a hydrophilic group

and a hydrophobic group and obtained by cleaving a polymer compound having the above described hydrophilic group and the above described hydrophobic group in a manner that the above described hydrophobic group is oriented in the surface side of the above described hydrophobic surface and the above described hydrophilic group is oriented in the direction different from that of the hydrophobic group.

Another aspect of an element having a reformed surface by the present invention is an element having a hydrophobic surface which is reformed to be a hydrophilic surface and to which fractionalized products comprising a hydrophilic group and a hydrophobic group and obtained by cleaving a polymer compound having the above described hydrophilic group and the above described hydrophobic group are stuck in a manner that the above described hydrophobic group is oriented in the surface side of the above described hydrophobic surface and the above described hydrophilic group is oriented in the direction different from that of the hydrophobic group.

A surface treatment solution to be used for the surface reforming according to the present invention is a surface treatment solution to be used for a surface reforming method for carrying out surface reforming by supplying a functional group for reforming to a partial surface to be reformed composing at least a part of the

surface of a prescribed element and is characterized by containing a polymer provided with a first part having a functional group and a second part having the interfacial energy different from that of the above described functional group and approximately equal to the surface energy of the above described partial surface, a volatile solvent having sufficient wettability to the above described element and being a good solvent to the polymer, and a cleaving catalyst of the above described polymer.

The surface treatment solution may further contain a volatile solvent having no wettability to the above described element and being a good solvent to the above described polymer. A method of producing such a surface treatment solution is characterized by dissolving the above described polymer in a volatile solvent having sufficient wettability to the above described element and being a good solvent to the above described polymer and then mixing a volatile solvent having no wettability to the above described element and being a good solvent to the above described polymer to the resultant solution.

Another aspect of a surface reforming method according to the present invention is a surface reforming method for carrying out surface reforming for a partial surface of an element and is characterized by reforming the surface by carrying out, on the above

described partial surface, condensation polymerization of ring-opened polymers oriented based on the affinity of the interfacial energy of a group similar to the surface energy of the partial surface of the element.

Another aspect of a surface reforming method according to the present invention is a surface reforming method for carrying out surface reforming for a partial surface of an element using a liquid-phase polymer and is characterized by involving a condensation step to be carried out on the above described partial surface by condensation polymerizing fractionalized products of a polymer comprises a first group having a functional group possible to be ring-opened and condensation polymerizable and a second group having an interfacial energy approximately equal to the surface energy of the partial surface of the element.

Another aspect of an element of the present invention is an element which has a surface comprising at least an olefinic resin and reformed by being made hydrophilic and is characterized by having a liquid-contacting surface structure having practically reciprocally a hydrophilic group with a relatively long chain and a hydrophobic group with a relatively short chain on the above described element surface and formed by forming an element surface coated with a treatment solution containing a polymer having the hydrophilic

group and a group with an interfacial energy approximately equal to the surface energy of the element surface comprising at least the above described olefinic resin as a constituent component, a diluted sulfuric acid as a cleaving catalyst of the above described polymer, and an alcohol, evaporating the treatment solution coating the above described element surface and simultaneously concentrating the diluted sulfuric acid to be a concentrated sulfuric acid on the above described element surface to ring-open the above described polymer, and then condensation-polymerizing the ring-opened products.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B are schematic figures illustrating the adhesion state of a polymer as a surface reforming agent formed on the object surface to be reformed of an element (a substrate) to the element surface in a surface treatment method of the present invention and FIG. 1A is a figure illustrating the case where a polymer has a first group as a functional group and a second group for adhering to the element surface both in the side chains and FIG. 1B is a figure illustrating the case where the second group is contained in the main chain;

FIG. 2 is a schematic figure illustrating the state of applying a treatment solution containing a

polymer as a surface reforming agent and forming a coating layer on the substrate in a surface reforming method of the present invention;

FIG. 3 is a generalized figure illustrating the step of partially removing a solvent in the coating layer formed on a substrate and containing a polymer as a surface reforming agent in a surface reforming method of the present invention;

FIGS. 4A and 4B are generalized figures illustrating the step of partial dissociation of a polymer as a surface reforming agent caused by an acid added to a treatment solution following the step of partially removing a solvent in the coating layer containing the polymer as a surface reforming;

FIG. 5 is a generalized figure illustrating the step of orienting a polymer as a surface reforming agent or its dissociated and fractionalized products following the step of further removing a solvent in the coating layer containing the polymer as a surface reforming agent;

FIG. 6 is a generalized figure illustrating the step of orienting a polymer as a surface reforming agent or its dissociated and fractionalized products and sticking and fixing them on the surface following the step of drying and removing a solvent in the coating layer;

FIG. 7 is a generalized figure illustrating the

step of re-bonding dissociated and fractionalized products one another derived from a polymer as a surface reforming agent, which is stuck, and fixed to and on the surface, by condensation reaction;

FIG. 8 is a generalized figure illustrating an embodiment of a surface reforming method of the present invention applied to a hydrophobic surface to convert the surface to be hydrophilic and showing the effect of adding water to a treatment solution;

FIGS. 9A and 9B are schematic figures illustrating an embodiment of a surface reforming method of the present invention applied to the treatment of making a hydrophobic PP container inner wall face be hydrophilic and FIG. 9A is a schematic figure illustrating the untreated inner wall face of the PP container and FIG. 9B is a schematic figure illustrating the inner wall face coated with a hydrophilic agent following the treatment of providing hydrophilicity;

FIGS. 10A, 10B, 10C and 10D are figures illustrating a PE/PP fibrous body usable for an ink absorbent in an ink tank, FIG. 10A is a schematic figure illustrating the utilization embodiment as an ink absorbent in an ink tank and FIG. 10B, FIG. 10C, and FIG. 10D are schematic figures respectively illustrating the whole shape of the PE/PP fibrous body and the orientation direction F1 of the fibers and the direction F2 rectangular to the direction F1, the above

described PE/PP fibrous body in the state before formation by thermal fusion, and the above described PE/PP fibrous body in the state after formation by thermal fusion;

FIGS. 11A and 11B are figures illustrating one example of a cross section structure of a PE/PP fibrous body shown in the FIGS. 10A to 10D and FIG. 11A is an example of approximately concentrically coating a PP core material with a PE sheath material and FIG. 11B is a schematic figure illustrating the example of eccentrically coating a PP core material with a PE sheath material;

FIGS. 12A, 12B, 12C, 12D, 12E and 12F are figures illustrating an embodiment of application a surface reforming method of the present invention to the treatment for making hydrophobic surface of the PE/PP fibrous body shown in FIGS. 10A to 10D be hydrophilic and FIG. 12A is a schematic figure of an untreated fibrous body, FIG. 12B schematically illustrates the step of immersing the fibrous body in a treatment solution for making the surface be hydrophilic, and FIG. 12C schematically illustrates the step of pressurizing the fibrous body after immersion and removing the excess treatment solution. FIGS. 12D to 12F are partially magnified figures of FIGS. 12A to 12C, respectively;

FIGS. 13A, 13B, 13C, 13D, 13E and 13F are figures

illustrating the steps successive to the steps illustrated in FIGS. 12A to 12C and FIG. 13A is a schematic figure illustrating the coating layer formed on the surface of a fibrous body, FIG. 13B schematically illustrates the step of drying and removing a solvent contained in the coating layer, and FIG. 13C is a schematic figure illustrating the coating on the surface of the fibrous body with an agent for making the surface hydrophilic. FIGS. 13D to 13F are partially magnified figures of FIGS. 13A to 13C, respectively;

FIG. 14 is a SEM photograph of 150 magnifications substituting the figure illustrating untreated PP-PE fibrous shapes and their surface state of a reference example (an untreated PP-PE fibrous absorbent);

FIG. 15 is a SEM photograph of 500 magnifications substituting the figure illustrating untreated PP-PE fibrous shapes and their surface state of a reference example (an untreated PP-PE fibrous absorbent);

FIG. 16 is a SEM photograph of 2,000 magnifications substituting the figure illustrating untreated PP-PE fibrous shapes and their surface state of a reference example (an untreated PP-PE fibrous absorbent);

FIG. 17 is a SEM photograph of 150 magnifications substituting the figure illustrating acid-treated PP-PE fibrous shapes and their surface state of a comparison

example 4 (PP-PE fibrous absorbent treated only with an acid and an alcohol);

FIG. 18 is a SEM photograph of 150 magnifications substituting the figure illustrating treated PP-PE fibrous shapes and their surface state of an example 2 (a PP-PE fibrous absorbent treated to be hydrophilic);

FIG. 19 is a SEM photograph of 500 magnifications substituting the figure illustrating treated PP-PE fibrous shapes and their surface state of an example 2 (a PP-PE fibrous absorbent treated to be hydrophilic);

FIG. 20 is a SEM photograph of 2,000 magnifications substituting the figure illustrating treated PP-PE fibrous shapes and their surface state of an example 2 (a PP-PE fibrous absorbent treated to be hydrophilic);

FIGS. 21A, 21B, 21C and 21D are figures illustrating an example of application of the surface reforming method of the present invention to the treatment of making the surface of a PP fine particle be hydrophilic and FIG. 21A is a schematic figure of an untreated PP fine particle, FIGS. 21B and 21C are respectively schematic figures illustrating the PP fine particle coated with an agent for making the surface hydrophilic by the treatment of making the surface hydrophilic, and FIG. 21D is a schematic figure illustrating the coating containing the agent for making the surface hydrophilic and formed on the

surface, which is a curved plane of the fine particle;

FIG. 22 is a schematic figure illustrating the step of stirring and drying a PP fine particle coated with a treatment solution by warm air blow;

FIG. 23 is a step figure illustrating one example of a manufacturing step of an element having a reformed surface by the present invention; and

FIG. 24 is a figure schematically illustrating one example of a presupposed distribution of a hydrophilic group and a hydrophobic group in the surface subjected to the surface reforming treatment by the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The surface modification method of the present invention allows the desired surface modification of an element by attaching a polymer (or finely fractionalized (fragmented) product thereof) to the surface the element has in a specific orientation while utilizing the functional group or the like which the molecule contained in the material constituting the element surface has, to impart the properties associated with the polymer (or finely fractionalized product thereof) to the surface.

The "element" used herein means the one made of various materials and taking a specific external shape. Therefore, it has an exposed external surface

associated with the external shape. Moreover, it may contain voids, cavities or hollows, each containing the section which is in communication with the outside. The internal surface (internal wall surface) which divides the section may be the partial surface to be treated by the surface modification method of the present invention. The hollow may have an internal surface by which it is fractionalized, and may be completely isolated from the outside. However, such a hollow can be subjected to the treatment by the present invention, so long as the surface treatment solution can be applied to its inside before the modification treatment and becomes isolated from the outside after the treatment.

The surface modification method of the present invention is applicable to any surface, out of all surfaces a varying element has, with which the surface treatment solution can be brought into contact with from the outside without damaging the element shape. The partial surface to be treated includes external surface of the element, internal surface in communication therewith, and both. Modification of properties of partial surface(s) selected and fractionalized from the surface to be treated is within the scope of the present invention. Depending on the selection, the embodiment of selecting the external surface of an element and its internal surface in

communication therewith is included in the modification of the desired partial surface region.

In the method of the present invention, a partial surface, i.e., at least a part of surface an element has, to be modified is treated. In other words, the surface of an element selected as required is treated partly or totally.

The element shape is not limited. It may be sheet-shaped, yarn-shaped, fibrous, spherical, particulate, tubular or in other shapes, including distorted one. The purpose of the element is also not limited. The surface modification method of the present invention is applied to an element in accordance with its specific purpose. The element is generally made of a material suitable for its purpose, e.g., plastic, resin, metal, glass, paper or leather which utilizes the natural material, or a material similar thereto, e.g., synthetic leather. The surface modification method of the present invention is applicable, in principle, to any surface of elements made of various materials.

The "surface an element has" used herein includes the surface the element itself originally has and the element surface treated by a certain method.

The "finely fractionalized polymer" used herein includes from the polymer fractionalized at its part to the monomer for the polymer. Viewed from the preferred

embodiments, it includes any type of polymer cleaved in the presence of a cleaving catalyst, e.g., acid. The "polymer made into film" includes a substantial film and film oriented differently region by region relative to the two-dimensional plane.

The principle of surface modification is described more concretely by taking modification of a surface comprising single material as the example, to facilitate explanation of the principle.

It is preferable that the "polymer" used herein comprises two sections, the first one having a functional group and second one having interfacial energy which is different from that of the functional group of the first section and almost equivalent to surface energy of the element to which it is to be attached, and that it is different from the material which constitutes the element surface. The desirable polymer may be adequately selected from those having interfacial energy almost equivalent to surface energy of the element to which it is to be attached, depending on the components of the element. It is more preferable that the "polymer" for this invention can be cleaved and subsequently condensed. It may have a functional group in addition to the two sections described above. In such a case, it is preferable, when hydrophilicization treatment is taken as an example, that the hydrophilic group as the functional

group is of longer chain than any functional group other than that in the above first or second section, which is more hydrophobic than the above hydrophilic group.

The portion to be surface-treated by the present invention may be composed of a single material or composite material of two or more types of materials, and also may be of a polymer different from the constituent of the element in consideration of material for the surface to be treated.

(Principle of surface modification)

Surface modification of an element by the present invention is effected by utilizing a polymer serving as the surface modifier which comprises the main skeleton (generic term for one or more groups in the main or side chain) to which a group is bound, the main skeleton having interfacial energy almost equivalent to surface (interfacial) energy of the element surface (substrate surface) and the group having interfacial energy different from surface (interfacial) energy of the element surface, wherein the main skeleton helps the polymer attach to the element surface while the group helps form the polymer film (coating layer) orienting outward from the element surface.

The polymer serving as the surface modifier for the present invention, when viewed from a different angle, has two types of groups, the first one having

affinity essentially different from that of the group exposed to the element surface before modification, and the second one having affinity essentially similar to that of the exposed group and being contained in the repeating unit in the main skeleton.

FIGS. 1A and 1B schematically illustrate the representative orientation types, FIG. 1A modeling a polymer with the first group 1-1 and second group 1-2 bonded as the side chains to the main chain 1-3 of the surface modifier, while FIG. 1B a polymer with the second group 1-2 constituting the main chain 1-3 itself and the first group 1-1 constituting the side chain.

In the orientation shown in FIGS. 1A and 1B, the outermost (outside) surface of the substrate 6, which constitutes the surface of the element to be surface-modified, has the first group 1-1, having interfacial energy different from surface (interfacial) energy of the substrate 6, oriented on the surface. As a result, the properties associated with the first group 1-1, having interfacial energy different from surface (interfacial) energy of the substrate 6, are utilized to modify the element surface. It should be noted that surface (interfacial) energy of the substrate 6 is determined by the material/molecule which constitutes the surface and group 5 exposed to the surface. More concretely, in the example shown in FIGS. 1A and 1B, the first group 1-1 works as the functional group for

surface modification to make the substrate 6 surface hydrophilic, when the substrate 6 surface is hydrophobic and first group 1-1 is hydrophilic. When the first group 1-1 is hydrophilic and group 5 exposed to the surface on the side of substrate 6 is hydrophobic, e.g., when polysiloxane is used as described later, it is considered that the conditions shown in FIG. 24 are present on the substrate 6 surface. Under these conditions, it is possible to adjust, when water or aqueous solution mainly comprising water is passed over the modified substrate 6 surface, the flow conditions or rate at which water or aqueous solution is passed by adjusting the balance between the hydrophilic and hydrophobic groups on the surface of substrate 6 modified. Such a surface structure allows to alternately arrange the functional group supplied from the polymer P and the other group having properties different from those of the functional group on the substrate surface (element surface to be treated), to produce the above effect when the functional group is hydrophilic and the other group is hydrophobic.

These surface conditions may be produced suitably by the methods used for Examples later described, although not limited thereto. These conditions may be suitably applied to a variety of materials and elements, e.g., tubes and vessels for handling liquid, to produce the above effect by adjusting the balance

between the hydrophilic and hydrophobic groups. In such a case, the functional group can have a longer chain than the other group.

In particular, when the element surface structure is fibrous or the like as shown in FIG. 24, the hydrophilic group 1-1 is a polymer group and is longer than the methyl group (hydrophobic group) in the side chain on the same side. Therefore, when an aqueous solution is passed over the element, the hydrophilic group 1-1 slants toward the element surface (or inner plane) under the influence of the flow rate (and, at the same time, substantially cover the methyl group). As a result, resistance to flow is greatly decreased. Conversely, when the aqueous solution is to be held over the element surface, the hydrophilic group 1-1 stands against the solution, i.e., oriented in the direction perpendicular to the element surface (or inner plane), as a result of which the methyl group is exposed to the fiber surfaces, making hydrophilicity predominant over hydrophobicity at the intra-molecular level. Therefore, a sufficient quantity of the solution can be held. The polymer preferably has many (at least two or more) hydrophilic groups, to secure the function of the hydrophilic group 1-1. This is illustrated by Example which uses polyoxyalkylene-poly(dimethyl siloxane) having the hydrophilic group 1-1 with a number of -C-O-C- bonds and OH group as the

terminal group. When the polymer has the methyl group replaced by another hydrophobic group, the hydrophilic group preferably has a higher molecular weight than the hydrophobic group, to occupy a larger space. In other words, it is preferable that a balance is produced in such a way that hydrophilicity is predominant over hydrophobicity.

The surface structure coming into contact with water in the present invention is applicable, as required, to the balanced hydrophilic and hydrophobic groups handling liquid other than water. For example, the element may be coated with a polymer P having the longer-chain hydrophilic group and shorter-chain hydrophobic group arranged alternately for the surface coming into contact with a liquid to be held over the surface.

When the substrate 6 is of polypropylene and polymer P is polyoxyalkylene-poly(dimethyl siloxane), the group 5 exposed to the substrate 6 surface is methyl ($-CH_3$) group, and the substrate 6 has surface energy of approximately 23 dyn/cm, due to the methyl group which has surface energy of approximately 23 dyn/cm. The poly(dimethyl siloxane) section of the polymer P of polyoxyalkylene-poly(dimethyl siloxane), having methyl ($-CH_3$) group facing the outside, has surface energy of approximately 23 dyn/cm. It is almost equivalent to that of the substrate 6, due to

methyl group.

The polyoxyalkylene of polyoxyalkylene-poly(dimethyl siloxane) has higher surface energy than the substrate 6, due to -OH group as the terminal group (surface energy: 42 to 44 dyn/cm) and oxyalkylene chain ($-CH_2-O-CH_2-$).

Therefore, when the substrate 6 is of polypropylene and polymer P is polyoxyalkylene-poly(dimethyl siloxane) (shown in FIGS. 1A and 1B), the poly(dimethyl siloxane) section serves as the main chain 1-3, methyl group in the poly(dimethyl siloxane) section as the second group 1-2, and polyoxyalkylene section as the first group 1-1 (side chain).

One of the methods for producing the element having the modified surface shown in FIGS. 1A and 1B is concretely described. It uses an improver which is a good solvent for the polymer as the surface modifier and improves wettability of the treatment agent with the substrate. This method spreads the treatment solution (surface modifier solution) 8, in which the polymer as the surface modifier is uniformly dissolved, over the substrate surface, and orients the polymer as the surface modifier as described above, while removing the solvent in the treatment solution 8.

More concretely, a surface treatment solution is prepared by dissolving a given quantity of the polymer and cleavage catalyst in a solvent which is a good

solvent for the polymer and sufficiently wettable with the substrate surface. It preferably contains pure water, when the functional group serves as the hydrophilic group. The substrate is coated with the above solution on the surface, and treated by evaporation/drying (e.g., in an oven at 60°C) to remove the solvent in the surface treatment solution.

It is preferable for the present invention to use an organic solvent which is sufficiently wettable with the substrate 6 surface and, dissolves the polymer P as the surface modifier, in order to facilitate uniform coating of the surface with the polymer for the surface modification. One of its other effects is to keep the polymer P uniformly dispersed in the liquid layer spread over the surface and sufficiently dissolved therein, even it is concentrated as the solvent is evaporated. In addition, the polymer P as the surface modifier is uniformly spread over the substrate 6 surface, because of sufficient wettability of the surface treatment solution with the surface, with the result that the surface is uniformly coated with the polymer, even it has a complex shape.

The surface treatment solution 8 may be prepared by two types of solvents, the first one being wettable with the substrate 6 surface, volatile and a good solvent for the polymer P, and the second one, although being a good solvent, less wettable with the substrate

6 surface and less volatile than the first one. One of the examples is a combination of isopropyl alcohol and water, described later, for the polyolefin-based resin serving as the surface for the substrate, which is coated with polyoxyalkylene-poly(dimethyl siloxane) as the polymer.

Addition of an acid 7 as the cleavage catalyst to the surface treatment solution is considered to bring about the following effects. For example, during the evaporation/drying step of the surface treatment solution, the acid component increases in concentration as the solution components evaporate. The acid of increased concentration under heating accelerates partial decomposition (cleavage) of the polymer P as the surface modifier and production of the finely fractionalized polymer P, allowing them to be oriented in the finer portions on the substrate 6 surface. Another effect is expected. Recombination of the cleaved sections of the polymer P during the final stage of the evaporation/drying step accelerates formation of the film (coating) of the polymer produced as a result of the recombination, preferably the monomolecular film.

Still another effects is expected, cleaned substrate 6 surface. The acid component of increased concentration, as a result of evaporation of the solvent during the evaporation/drying of the surface

treatment solution 8, more efficiently removes impurities from the substrate 6 surface and the vicinity thereof, to clean the substrate 6 surface. The cleaned surface is expected to promote physical adhesion between the substrate material/molecules and polymer as the surface modifier.

The acid of increased concentration under heating partly decomposes the substrate surface, producing the active sites thereon, which may cause the auxiliary reactions between these sites and finely fractionalized (cleaved) polymer, described above. Depending on conditions, chemical adsorption of the auxiliary surface modifier on the substrate partly helps stabilize adhesion of the surface modifier to the substrate.

The main skeleton of the surface modifier (including the hydrophilicization treatment solution 8), having surface energy almost equivalent to that of the substrate 6, is cleaved, and the resultant finely fractionalized parts are condensed with each other to form a polymer film on the substrate 6 surface. Formation of the polymer film is explained by referring to FIGS. 2 to 8 for the case where the functional group 1-1 is hydrophilic to impart hydrophilicity to the hydrophobic substrate surface. The hydrophilic group means the one having a structure which can impart hydrophilicity as the whole group. It includes a

hydrophilic group itself, and even a group having a hydrophobic chain or hydrophobic group, so long as it is substituted with a hydrophilic group or the like to be serviceable as a group capable of imparting hydrophilicity.

FIG. 2 is an enlarged view illustrating the hydrophilicization treatment solution 8 spread over the substrate surface. At this stage, the polymers P1 to P4 as the hydrophilicization agent in the hydrophilicization treatment solution 8 and acid 7 are uniformly dissolved in the hydrophilicization treatment solution 8 over the substrate 6 surface. FIG. 3 is an enlarged view illustrating the drying step for the hydrophilicization treatment solution spread over the substrate surface. During the drying step under heating, the acid 7 component increases in concentration as a result of evaporation of the solvent to more efficiently remove impurities from the substrate 6 surface and vicinity thereof. This effect of cleaning the substrate 6 surface exposes the pure substrate 6 surface, to promote physical adhesion between the substrate 6 surface and polymer P1 to P4 as the surface modifier. At the same time, the acid 7 component increased in concentration, as a result of evaporation of the solvent under heating during the drying step for the hydrophilicization treatment solution 8 spread over the substrate 6 surface,

accelerates partial cleavage of the polymer P1 to P4 as the hydrophilicization agent.

FIGS. 4A and 4B schematically illustrates decomposition of the polymer P1 by the concentrated acid 7. As shown in FIG. 4A, the concentrated acid 7 acts on the polymer P1, to cleave the main skeleton 1-3 into the fractionalized products P1a and P1b as shown in FIG. 4B. FIG. 5 illustrates adsorption of the fractionalized hydrophilicization agent on the substrate 6. The main skeleton (having surface energy almost equivalent to that of the substrate 6) of the fractionalized products of P1a to P4b from the polymer P constituting the hydrophilicization agent are selectively oriented on the pure substrate 6 surface exposed as a result of the cleaning, as the solvent evaporates and the fractionalized products reach a saturation concentration in the solution. As a result, the group 1-1 (having surface energy different from that of the substrate 6) in the surface modifier outside of the substrate 6 is oriented toward the substrate.

Thus, on the surface of the substrate 6 the main skeleton of the fractionalized polymers P1a to P4b having surface energy almost equivalent to that of the substrate 6 are oriented, and group 1-1 having surface energy different from that of the substrate 6 is oriented outward, thus in the opposed direction to the

substrate 6 surface. Therefore, when the group 1-1 is hydrophilic, the substrate 6 surface becomes hydrophilic and is modified. FIG. 6 schematically illustrates the hydrophilicization agent adsorbed on the substrate surface, after the former is spread and dried.

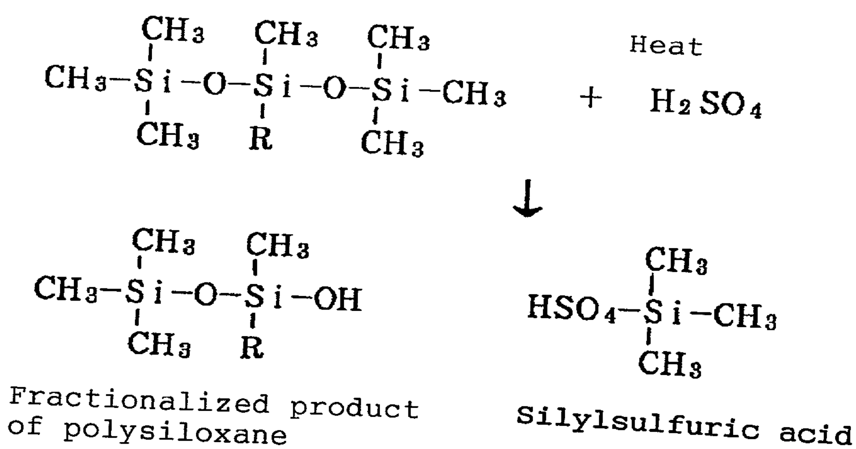
When a specific polymer, e.g., polysiloxane, is used, fractionalized products P1a to P4b are recombined with each other at least partly by condensation, to produce the polymer of higher molecular weight through the bonds (recombination sites C formed by condensation). This can increase strength of the coating film of the hydrophilicization agent. When polysiloxane is used, the siloxane section may be dissociated by the concentrated acid 7, after it is adsorbed by the substrate 6 surface, to be condensed with moisture 11 in air 9 through the recombination sites C, further stabilizing the adsorbed conditions. FIG. 7 schematically illustrates the recombination by condensation of the dissociated siloxane section with moisture 11 in air. The mechanisms involved in the cleavage to form the fractionalized products and their recombination to produce the condensed polymer P1A to P3A are explained below for the case of polysiloxane as the polymer.

The dilute acid 7 increases in concentration in the surface treatment solution 8 as the solution spread

over the surface to be treated is dried in a controlled manner. The concentrated acid 7 (e.g., H_2SO_4) cleaves the siloxane bond in polysiloxane into the fractionalized polysiloxane products and silylsulfuric acid (Scheme 1). These fractionalized products increase in concentration in the surface treatment solution 8 as the solution spread over the surface to be treated is further dried, increasing probability of contact between them. As a result, the fractionalized products undergo condensation with each other, to reproduce the siloxane bonds (Scheme 2). The methyl group in the silylsulfuric acid as the by-product is oriented toward the surface to be treated, when the surface is hydrophobic, and the sulfone group is oriented in the direction different from that of the surface, conceivably providing some contribution to hydrophilicization of the surface.

[General formula 1]

Scheme 1



Scheme 2

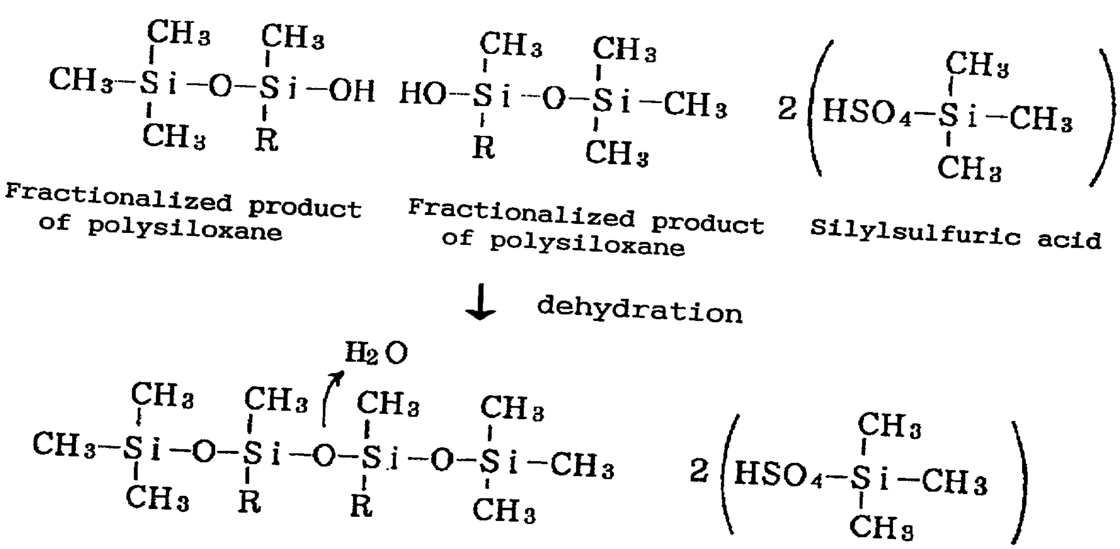


FIG. 8 schematically illustrates one example of conditions of the surface treatment solution, when it is of a composition with water (water-containing layer 12) in the solvent. When water is present in the solvent for the treatment solution which hydrophilicizes the surface under heating, evaporation of the solvent is accompanied by evaporation of water and the volatile organic solvent (10: vapor of volatile organic solvent, and 11: vapor of water). During this step, since the volatile organic solvent is evaporated faster than water, water is concentrated in the solution, to increase surface tension of the solution. This produces a differential surface energy in the interface between the substrate 6 surface to be treated and treatment solution. The section having surface energy almost equivalent to that of the substrate 6 in the fractionalized products P1a to P4b from the polymer as the hydrophilicization agent is oriented toward the substrate 6 surface to be treated in the interface between the substrate 6 surface to be treated and treatment solution whose water content increases as a result of evaporation (water-containing layer 12). At the same time, the section having the hydrophilic group 1-1 in the fractionalized products P1a to P4b from the polymer as the hydrophilicization agent is oriented toward the water-containing layer 12 whose water content increases as a result of evaporation of the

organic solvent. As a result, it is considered that the given orientation of the fractionalized products of the polymer is further improved.

The present invention is applicable to various elements and purposes, depending on the characteristics and types of the functional groups in the polymers used for surface modification.

(1) When the functional group is hydrophilic

The elements whose surface is modified by the method of the present invention include water-absorptive ones, e.g., paper diapers, sanitary napkins, ink absorbers for ink jet systems, and used ink absorbers (prepared by the method illustrated by one of the preferred embodiment described above, when the element contains olefin-based fibers), which can be surface-modified by the present invention to be sufficiently hydrophilic to instantaneously absorb liquid. The present invention is also useful for the elements required to hold liquid. The present invention is also applicable to pigment particles used as an ink colorant. When the particles are surface-modified by the method of the present invention, they may be well dispersed in water without using a dispersant. The fishery tools, e.g., fishing nets and lines, can reach a target point more quickly after thrown in water, when surface-modified by the method of the present invention, because they are more compatible

with water.

(2) When the functional group has affinity for oil

The present invention can impart the required functions to those elements required to have affinity for oil at the portion in contact with oil, e.g., oil cans and transportation tanks.

(3) When the functional group is liquid-repellent (e.g., hydrophobic group)

The present invention can expand functions of liquid-repellent liquid (whether it is water or oil) for various elements, e.g., washing stand and kitchen sinks, walls, roads, mirrors, automobile exteriors or the like, and glass surfaces, at the molecular level, or even decrease these functions to desired levels, by controlling types of the functional groups or their numbers at unit molecule.

(4) When the functional group is polar

The present invention can provide the elements with a filter function (by utilizing anodic properties for ion-exchanging or removal of impurities), or an adduct function by chemically reacting the element with a certain reactive group. In particular, when the filter composed of a number of fibers is formed by an olefinic polymer, the present invention can provide the filter with desired characteristics while making it treatable by incineration and hence environmentally favorable, as illustrated by one of the preferred

embodiments described above.

The present invention also gives the element which can develop a color or emit light, when a colorant or fluorescent agent reactive with the polar group and adsorptive is used.

The present invention greatly expand the range of these desired characteristics, and can find limitless applicable areas.

(5) When the functional group has no characteristics the element is required to exhibit, but is used to form a uniformly thin film

In this case, the functional group is required to have interfacial energy different from that of the group on the side adsorbed on the polymer surface as the sole essential condition. It can improve orientation of the group to the sections having almost equivalent interfacial energy and surface energy. It is preferable, in this case, that the polymer is cleaved at least partly to cope with more diversified surface conditions. It is more preferable that the fractionalized structure resulting from the cleavage (monomer, dimer, trimer or polymer having an intermediate molecular weight) is recombined with each other by condensation or crosslinking to form a polymer of higher molecular weight to improve the adhesiveness.

The element provided with these characteristics by the present invention for its entire peripheries or

surfaces has the structure surface itself forming the strong film, and becomes more durable.

(6) The present invention is applicable to any other area, so long as the element has improved characteristics by one or more of the mechanisms described above. All of these elements are included in the present invention.

The present invention provides especially excellent effects, when it uses a treatment solution containing a wettability improver capable of improving wettability to the element surface and that the solvent of the polymer is attainable (e.g., isopropyl alcohol, IPA), solvent accelerating cleavage of the polymer, one of the functional groups described above, and the polymer having interfacial energy different from that of the functional group and almost equivalent to partial surface energy of the element surface. The surface modification, effected by the cleavage and subsequent condensation, exhibits particularly excellent effects and securely gives uniformity and characteristics which cannot be provided by the conventional method.

FIG. 23 illustrates one of the process examples for producing these elements. This process comprises a series of steps; supply of the element to be treated and treatment solution (processing liquid) as the first step (S1), application of the treatment solution to the

element surface to be treated (S2), removal of surplus materials from the surface to be treated (S3), concentration/evaporation of the treatment solution for cleavage of the polymer and orientation of the fractionalized products on the surface to be treated (S4), condensation for recombining the fractionalized products with each other to produce the polymer (S5), and production of the element with modified surfaces (S6).

The treatment solution concentration/evaporation step (S4) is preferably effected by a continuous heating/drying step at higher than room temperature but at or lower than boiling point of the solvent (e.g., 60°C) for a varying time, e.g., approximately 45 minutes to 2 hours when polysiloxane having a hydrophilic group is used together with water, an acid and organic solvent (e.g., isopropyl alcohol) for modifying the surface composed of a polyolefin-based resin, and around 2 hours when a 40 wt.% aqueous solution of isopropyl alcohol is used. The drying treatment time may be reduced by decreasing water content.

In the example shown in FIG. 23, the fractionalized products are formed by cleavage of the polymer on the element surface to be treated. However, the treatment solution containing the fractionalized products beforehand may be spread over the element

surface to be treated, to orient them thereon.

As described above, the treatment solution composition useful for the present invention comprises, e.g., a wettability improver which has wettability with the surface to be modified for making the treatment solution more wettable with the surface to be treated and, at the same time, works as a good solvent for the surface modifier; solvent; polymer-cleaving catalyst; and polymer which contains a functional group for imparting the modification effect to the surface to be modified and another group for imparting adhesive function to the surface to be modified.

Examples

The surface modification method of the present invention, element surface modified by the method, and evaluation thereof are described more concretely by Examples. It is to be understood that Examples are to provide some of the preferred embodiments and not to limit the present invention.

(Example 1)

This example applied the present invention to modification of the internal hydrophobic wall surfaces of a polypropylene container 90 to be hydrophilic, as illustrated in FIG. 9A.

The hydrophilicization treatment solution having a composition given in Table 1 was prepared.

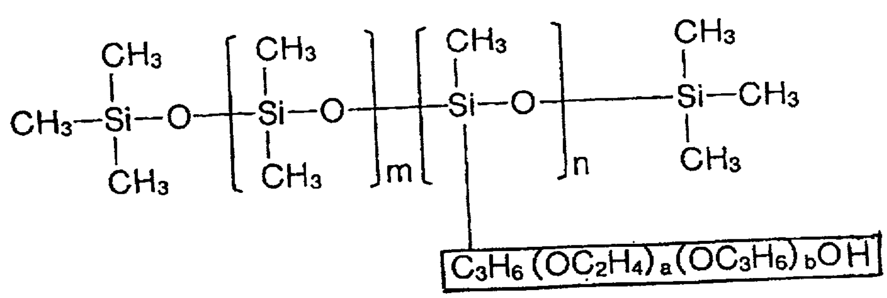
[Table 1]

(Hydrophilicization treatment solution composition)

Components	Contents (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	4.0
Sulfuric acid	0.5
Isopropyl alcohol	95.5

The solution was prepared using isopropyl alcohol as an organic solvent alcohol well dissolving polyoxyalkylene-poly(dimethyl siloxane) as the polymer. Isopropyl alcohol was first well mixed with sulfuric acid as an inorganic acid added to 0.5 wt.% as concentrated sulfuric acid concentration in the final solution. Then, polyoxyalkylene-poly(dimethyl siloxane) as the polymer was added to the above mixture to 4.0 wt.% as polymer concentration in the final solution, and uniformly dissolved therein, to prepare the hydrophilicization treatment solution. Polyoxyalkylene-poly(dimethyl siloxane) used for Example 1 is shown by the general formula (1):

[General formula 2]



where, (m) and (n) are each a positive integer; (a) and

(b) are also each a positive integer; and R is an alkyl or hydrogen. The polymer has a structure of poly(dimethyl siloxane) with one of the methyl group in the main repeating unit being substituted by polyoxyalkylene group. The commercial product (Nippon Unicar, silwet L-7002™) was used. The section enclosed by a rectangle in the general formula (1) is a hydrophilic group, which corresponds to the first group (functional group) in FIGS. 1A and 1B and group 1-1 in FIG. 24.

The above treatment solution dissolves a small quantity of water molecules, associated with concentrated sulfuric acid, in addition to the sulfuric acid molecules.

The treatment was attempted to make hydrophilic the inner wall surfaces of a polypropylene (PP) container 40 shown in FIG. 9A with the above hydrophilicization treatment solution. A small quantity of the hydrophilicization treatment solution prepared was put in the PP container of 50 ml in inner volume, to wet the container inner surfaces with the hydrophilicization treatment solution. The container was turned upside down and shaken, after the inner surfaces were uniformly wetted, to release the surplus solution. The container whose inner surfaces were wetted with the coating film 48 of the hydrophilicization treatment solution was dried in an

oven at 60°C for 1 hour. This produced the hydrophilicization-treated PP container 40A, shown in FIG. 9B.

(Comparative Examples 1 to 3)

The three types of solutions having the following compositions were prepared, and the treatment was attempted for the inner wall surfaces of a polypropylene (PP) container with each of these solutions, to verify the hydrophilicization treatment effects brought by the present invention.

(1) Solution composition for Comparative Example 1

Comparative Example 1 used the hydrophilicization-treatment solution composition shown in Table 1, except that it comprised only isopropyl alcohol and sulfuric acid. In other words, the solution for Comparative Example 1 was free of polyoxyalkylene-poly(dimethyl siloxane), which was used to form the desired polymer coating film by the present invention.

(2) Solution composition for Comparative Example 2

Comparative Example 2 used the hydrophilicization-treatment solution composition shown in Table 1, except that it comprised only isopropyl alcohol and polyoxyalkylene-poly(dimethyl siloxane). In other words, the solution for Comparative Example 2 was free of concentrated sulfuric acid and a small quantity of the water molecules associated therewith.

(3) Solution composition for Comparative Example 3

Comparative Example 3 used the hydrophilicization-treatment solution composition shown in Table 1, except that isopropyl alcohol was replaced by hexane, which is a bad solvent for polyoxyalkylene-poly(dimethyl siloxane).

A small quantity of each of the above solutions was put in the PP container of 50 ml in inner volume, to wet the container inner surfaces in a manner similar to that for Example 1. Each container was turned upside down and shaken, after the inner surfaces were uniformly wetted, to release the surplus solution. The container whose inner surfaces were wetted was dried in an oven at 60°C for 1 hour. The untreated PP container was also used in Reference Example.

Each PP container was evaluated whether its treated surface conditions were satisfactory or not. The evaluation methods and results are described below.

a) Method for evaluating hydrophilicity of the PP container

The inner surfaces of a total of 4 PP containers, treated with the solution for Example 1 or Comparative Examples 1, 2 or 3, and the untreated one (Reference Example) were rinsed with pure water. Each container was filled with fresh pure water to approximately one-third of the inner volume, after rinse water was discarded, and lightly shaken, to visually confirm conditions of pure water attaching to the inner wall

surface of the container.

b) Evaluation results of hydrophilicity of the PP container

The inner surface of the PP container hydrophilicization-treated in Example 1 was wetted with pure water, with the conditions of the untreated PP container for Reference Example as the reference. By contrast, those of the PP containers treated with the solution prepared by Comparative Example 1, 2 or 3 were not wetted at all, because pure water was observed to trickle down in droplets.

Each of them clearly had the hydrophobic inner surface, as was the case with the one for Reference Example.

The solutions for Comparative Examples 2 and 3 contained polyoxyalkylene-poly(dimethyl siloxane), which, however, was not effectively adsorbed by the PP surfaces. As a result, it was washed off when the treated containers were rinsed with pure water immediately before they were evaluated.

By contrast, the PP container treated in Example 1 was wetted with pure water after it was rinsed with pure water, indicating that polyoxyalkylene-poly(dimethyl siloxane) was fast adsorbed by the PP surface and it was effectively adsorbed.

These evaluation results indicate that the surface of plastic material can be effectively

hydrophilicization-treated with a solution containing a polyalkylsiloxane having a polyalkyleneoxide chain, acid and alcohol, spread over the PP container and dried. It is found that a polymer of polyalkylsiloxane can be oriented on and attached to the PP surface as aimed, when the surface is treated with the polymer in the presence of the alcohol and acid. It is also confirmed that a combination of the acid and alcohol also has an effect of cleaning the plastic surface, and that the cleaned surface coupled with the methyl group in the alkylsiloxane structure (as the repeating unit of the hydrophobic polyalkylsiloxane having a polyalkyleneoxide chain) oriented on the substrate surface improves overall adhesive power.

The polyalkylsiloxane having a polyalkyleneoxide chain can be uniformly dispersed on and effectively attached to the plastic surface, because it is dissolved in the alcohol as a good solvent therefor. When a hydrophilic surfactant only is spread over the plastic surface and dried thereon, the surface shows hydrophilicity only during the initial stage, which, however, is lost when the surface is rinsed with pure water, because the surfactant is dissolved and eluted out in water.

(Example 2)

Example 2 applied the surface modification method of the present invention to a fibrous element, more

concretely to an element of polypropylene/polyethylene (PP/PE) fibers for surface hydrophilicization treatment. The element of PP/PE fibers actually prepared was a block-shaped one in which the fibers were composited with each other to take a form useful for, e.g., an ink absorbing element which could absorb liquid (e.g., ink) and hold the used liquid. For example, referring to FIG. 10A, a container 21 having an adequate shape and open to air by an opening 25 can be used as a liquid-holding container 20, when it is filled with fibrous bodies 23, capable of functioning as an absorbing element 24 to absorb and hold various types of liquid (e.g., ink), oriented in a given direction. Such an ink-absorbing element 24 can be suitably used for a discharged ink tank for ink jet recorders.

More concretely, the fibrous element 23 which constituted the absorbing element 24 was composed of the biaxial fibrous element of polypropylene and polyethylene fibers, each approximately 60 mm long. This biaxial fibrous element was of a core-sheath structure, with a polypropylene fiber having a higher melting point as the core 23b encased by polyethylene having a lower melting point as the sheath 23a. FIG. 11A shows its section perpendicular to the axial direction, whose external shape (outer peripheral shape) was essentially circular (closed ring shape).

The fibrous blocks, each composed of the short fibers and having the above section, were arranged in the fiber axis direction in, and heated by, a cotton-carding machine, to fuse the fibers with each other. More concretely, they were heated at above melting point of polyethylene as the sheath 23a but below melting point of polypropylene as the core 23b, to have the structure with the sheaths 23a of polyethylene fusing each other at the points they came into contact with each other.

In the above fibrous structure 23, referring to FIG. 10B, the fibers 23A were arranged in the fiber axis direction in the cotton-carding machine and continuously arranged mainly in the longitudinal direction (F1). They came into contact with, or close to, each other at points, e.g., α, β, γ and ε, as shown in FIG. 10C. They were fused with each other under heating at the contact (intersection) points, e.g., at the points α, β, γ and ε, as shown in FIG. 10D, to form a network structure, giving the structure mechanical elasticity in the direction F2 perpendicular to the longitudinal direction F1. This was accompanied by increased tensile strength in the longitudinal direction F1 shown in FIG. 10B. The structure, although lower in tensile strength in the direction F2 than in F1, was elastic with restoring force against compressive stress in the direction F2.

Looking the fibrous structure 23 in more detail, referring to FIG. 10D, the individual fibers 23A were crimped, to help form complex network structures between the adjacent fibers, and fused with each other, e.g., at the points α, β, γ and ε. Some of the crimped fibers 23A were arranged in the direction F2 perpendicular to the longitudinal direction F1, to make the structure three-dimensional with the fibers fused with each other. The fibrous element 23 actually prepared in Example 2 was formed into a concentric sliver of biaxial fiber tows, shown in FIG. 11A, with a polypropylene fiber (melting point: around 180°C) as the core 23a encased in polyethylene(melting point: around 132°C). The fibrous element 23, composed of the fibers mainly oriented in the longitudinal direction F1, shows fluid conditions within the element and stationary liquid-holding conditions clearly different in the directions F1 and F2, when immersed in a liquid.

In this example, the element shape was of a fibrous structure, generally holding more liquid than the container with planar surfaces, e.g., that prepared by Example 1, and the treatment solution of the following composition was used:

[Table 2]

(Hydrophilicization treatment solution composition of fiber)

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	0.40
Sulfuric acid	0.05
Isopropyl alcohol	99.55

(1) Method for hydrophilicization-treatment of the absorption body of PP/PE fibers

The absorption body 24 of polypropylene/polyethylene fibers, having the fusion-treated structure shown in FIG. 12A, was immersed in the hydrophobicization treatment solution 28 of the above composition (FIG. 12B). The solution 28 was held in the voids between the fibers 23A for the fibrous absorption body 24, as shown in FIG. 12E as the magnified view of FIG. 12B. The fibrous absorption body 24 holding the solution 28 was pressed by a pressing jig 27, e.g., metallic mesh (FIG. 12C), to remove the surplus treatment solution 28 held in the voids between the fibers 23A, as shown in FIG. 12F as the magnified view of FIG. 12C. When the jig 27 was removed, the fibrous absorption body 24 returned back to the original shape, as shown in FIG. 13A, with the fibers 23A coated with the liquid layer 28A. The absorption body 24 with the fibers wetted with the

solution was dried in an oven 29 at 60°C for 1 hour (FIG. 13B). This produced the fibrous absorption body 24 with the fibers 23A coated with the hydrophilic layer 28B, as shown in FIG. 13C. FIGS. 12D to 12F are partially magnified views of respective FIGS. 12A to 12C, and FIGS. 13D to 13F are partially magnified views of respective FIGS. 13A to 13C.

(Comparative Example 4 and Reference Example 1)

In Comparative Example 4, the fibrous absorption body was hydrophilicization-treated in the same manner as in Example 2 except that the treatment solution comprised only sulfuric acid and isopropyl alcohol. In other words, the solution for Comparative Example 4 was free of polyoxyalkylene-poly(dimethyl siloxane). The untreated fibrous absorption body of PP/PE fibers was also used in Reference Example 1.

In Example 2, 0.5 g of the fibrous absorption body of PP/PE fibers was treated by the above-described treatment method with 0.3 to 0.5 g of the above hydrophilicization-treatment solution. Comparative Example 4 used the same quantity of the solution applied to the whole element using the above described application method.

Each fibrous absorption body thus prepared was evaluated whether its treated surface conditions were satisfactory or not. The evaluation methods and results are described below.

(1) Method for evaluating hydrophilicity of the fibrous absorption body of PP/PE fibers

a) Evaluation by pure water drops fallen from a dropper

Pure water drops were fallen from a dropper onto the fibrous absorption bodies of PP/PE fibers, prepared by Example 2 and Comparative Examples 4, and the untreated one (Reference Example), to observe extent of pure water sinking into the bodies.

b) Evaluation by immersion in pure water

The fibrous absorption bodies of PP/PE fibers, prepared by Example 2 and Comparative Examples 4, and the untreated one (Reference Example), were slowly placed on pure water, held by a container sufficiently large to accommodate the fibrous element, to observe extent of pure water sinking into the bodies.

(2) Results of evaluation of hydrophilicity of the fibrous absorption body of PP/PE fibers

(a) Results of evaluation by pure water drops fallen from a dropper

Pure water drops, fallen from a dropper onto the fibrous absorption body of PP/PE fibers prepared by Example 2, were observed to instantaneously sink into the element inside.

By contrast, pure water drops fallen from a dropper onto the fibrous absorption body of PP/PE fibers prepared by Comparative Example 4 and untreated one (Reference Example 1) were observed not to sink

into the element inside, but repelled to form droplets on the surfaces.

b) Results of evaluation by immersion in pure water

The fibrous absorption body prepared by Example 2 was slowly placed on pure water held by a container, and observed to slowly sink into water, indicating that its surfaces were hydrophilic.

By contrast, both the fibrous absorption body of PP/PE fibers prepared by Comparative Example 4 and untreated one (Reference Example 1), slowly placed on pure water held by a container, were observed to securely float on water. They showed no sign to absorb water thereafter, indicating that they were clearly hydrophobic.

These results indicate that the fibrous absorption body of PP/PE fibers can be also coated with a polyalkyl siloxane layer (hydrophilic layer) 28B, as shown in FIG. 13C, to be effectively hydrophilicization-treated, when the solution containing a polyalkyl siloxane having a polyalkylene oxide chain, acid and alcohol was spread over the element surface and dried. Therefore, it is found that the fibrous absorption body 24 of PP/PE fibers can have a sufficient function to serve as an element of absorbing aqueous ink.

The fiber surfaces were analyzed by a scanning electron microscope (SEM), in order to verify that the

surface modification method of the present invention attaches a polyalkyl siloxane having a polyalkylene oxide chain to the PP/PE fiber surface to form the polymer coating layer thereon.

FIGS. 14, 15 and 16 show the magnified SEM photographs of the untreated PP/PE fiber surfaces of the fibrous absorption body of Reference Example 1 (magnification: 150, 500 and 2,000, respectively). FIG. 17 shows the magnified SEM photograph of the PP/PE fiber surfaces of the fibrous absorption body of Comparative Example 4, treated with only the acid and alcohol (magnification: 150).

FIGS. 18, 19 and 20 show the magnified SEM photographs of the PP/PE fiber surfaces of the hydrophilicization-treated fibrous absorption body of Example 2 (magnification: 150, 500 and 2,000, respectively).

No structural changes considered to result from deposition of organic substance on the fiber surfaces are clearly shown in all of these magnified SEM photographs of the PP/PE fiber surfaces. Indeed, no difference is observed between the untreated PP/PE fiber surfaces (FIG. 16) and hydrophilicization-treated PP/PE fiber surfaces (FIG. 20) even by the 2000 times magnified SEM photographs. It is therefore judged that the hydrophilicization-treated PP/PE fibers are uniformly coated with a thin film (considered to be

monomolecular layer) of polyoxyalkylene-poly(dimethyl siloxane), showing appearances not differentiated from the untreated surfaces by the SEM analysis.

By contrast, the PP/PE fiber surfaces treated only with the acid and alcohol show the fiber intersections (fused sections) cut at many points and many knot-like sections in the fibers, as shown in the SEM photograph (FIG. 17). These changes are considered to result from deterioration of the PE/PP molecules on the fiber surfaces (in particular PE molecules in the surface layer) during the heating/drying step, accelerated by increased concentration of the acid as a result of evaporation of the solvent and heat itself for the drying step.

On the other hand, the hydrophilicization-treatment for the present invention causes no cutting at the fiber joints nor formation of knot-like sections in the fibers, which are observed in the PP/PE fiber surfaces treated only with the acid and alcohol, although it uses the treatment solution containing the same concentration of the acid and the same heating/drying step. This fact indicates controlled deterioration of the PE molecules on the fiber surfaces during the hydrophilicization-treatment for Example 2. It is considered, even when the acid acts on the fiber surfaces to cut the PE molecules and produce radicals within the molecules, that some materials and

structures capture the radicals to control destruction of the PE molecules by the chain reactions caused by the radicals. It cannot be ruled out that polyoxyalkylene-poly(dimethyl siloxane) attaching to the fiber surfaces is involved in the capture of the radicals to form the chemical bonds with the PE surfaces while capturing the radicals formed and thereby to control destruction of the PE/PP molecules by the radical-caused chain reactions.

Overall, it is judged that modification of the fiber surfaces is achieved in Example 2 by the thin film of polyoxyalkylene-poly(dimethyl siloxane) uniformly deposited on the fiber surfaces. The favorable side-effects during the hydrophilicization-treatment include cleaning of the fiber surfaces by the acid and solvent contained in the treatment solution, which possibly accelerates physical adsorption of the polyalkylene oxide chain. The chemical bonding between the PE molecules, cut by the acid of increased concentration and heat, and polyalkylene oxide chains can occur to no small extent.

The biaxial fiber may be eccentric, as shown in FIG. 11B, with the core section (core material) 23b partly exposed to the outer surface, as a result of which the fiber surfaces have the outer layer (sheath) 23a surfaces and core surfaces. The surface modification method of the present invention can impart

hydrophilicity to both the exposed core surfaces and sheath surfaces, even in such a case. When a hydrophilic surfactant only is spread over the surface and dried thereon, the surface partly shows hydrophilicity only during the initial stage, which, however, is lost when the surface is rinsed with pure water with lightly rubbing, because the surfactant is soon dissolved and eluted out in water.

(Example 3)

This example applied the present invention to hydrophilicization-treatment of plastic particle surfaces. More concretely, the polypropylene particle surfaces were treated in a manner similar to that for Example 1, which modified the water-repellent inner wall surfaces of the polypropylene container to be hydrophilic.

The hydrophilicization treatment solution having a composition given in Table 3 was prepared.

[Table 3]

(Hydrophilicization treatment solution composition)

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	4.0
Sulfuric acid	0.5
Isopropyl alcohol	95.5

The solution was prepared by the method similar to that for Example 1. Isopropyl alcohol was first well mixed with sulfuric acid added to 0.5 wt.% as concentrated sulfuric acid concentration in the final solution. Then, polyoxyalkylene-poly(dimethyl siloxane) was added to the above mixture to 4.0 wt.% as polymer concentration in the final solution, and uniformly dissolved therein, to prepare the above hydrophilicization-treatment.

(1) Hydrophilicization-treatment of polypropylene (PP) particles

The PP particles 31 used for Example 3 were spherical, having a diameter of 2 mm.

The PP particles 31 were immersed in the above hydrophilicization-treatment solution 38, and then scooped up to be separated from the solution. The PP particles 31 coated with the treatment solution 38 were put in a container 30 (FIG. 22), and hot wind was vigorously sent into the container 30, while stirring the particles 31 to prevent fusing these particles with each other. These particles were treated during this step by evaporating the solvent included in the treatment solution 38 and drying the particles. This treatment method is one of the preferred embodiments of the present invention, because of the favorable effects it brings; e.g., uniform coating and film-making resulting from rotation of the PP particles themselves

and surface tension around the spheres, to secure uniform coating.

(Reference Example 2)

The untreated PP particles were used for Reference Example 2.

The treated surface conditions were evaluated by the following methods for the PP particles treated for surface modification (Example 3) and untreated (Reference Example 2).

Method for evaluating hydrophilicity of the PP particles

(1) Evaluation by stirring with pure water

The PP particles, hydrophilicization treated for surface modification (Example 3) and untreated (Reference Example 2), were put in pure water held in a polyethylene container and stirred therein by a stirrer, to observe the particle conditions.

(2) Evaluation results of hydrophilicity of the PP particles

The results of evaluation by stirring with pure water are described. When the PP particles treated in (Example 3) were stirred in pure water, they were found to be dispersed and stirred in pure water. By contrast, the untreated PP particles (Reference Example 2) were scarcely dispersed in pure water, and found to be forced to move toward the polyethylene container walls and float on pure water.

The results indicate that the PP particles prepared by Example 3 were well surface-treated for hydrophilicization, as was the case with the container prepared by Example 1. This means that the untreated PP particle surfaces (shown in FIG. 21A were densely coated with the coating film 38A of polyoxyalkylene-poly(dimethyl siloxane), as shown in FIG. 21B. It is also confirmed that the method of the present invention is applicable not only to a flat plane (Example 1) but also to a curved surface, such as particle surface (Example 3), to easily form the polymer coating 38A as schematically shown in FIG. 21D. As shown, the ring-shaped polymer coating 38A on the surface periphery (closed ring-shaped section of the section periphery) to keep the surface-modified section not coming off easily. FIG. 21A is the section of the untreated PP particle, FIGS. 21B and 21C are the section of the hydrophilicization-treated PP particle and its partially magnified view, respectively, and FIG. 21D is the polymer film covering the outer periphery of the PP particle.

(Example 4)

Example 4 applied the method of the present invention to a fibrous element of propylene/polyethylene (PP/PE) fibers for surface modification with a solution containing poly(dimethyl siloxane) (amino-modified poly(dimethyl siloxane))

having amino group as the functional group.

More concretely, the fibrous element of PP/PE fibers was coated with amino-modified poly(dimethyl siloxane), by the procedure similar to that for Example 2, to modify the water-repellent polypropylene surface to be hydrophilic. The fibrous element of PP/PE fibers used in this example was the same as the one for Example 2.

This example used the same hydrophilicization treatment solution as that for Example 2, except that polyoxyalkylene-poly(dimethyl siloxane) was replaced by amino-modified poly(dimethyl siloxane).

[Table 4]

(Surface modification solution composition)

Components	Composition (wt.%)
Amino-modified poly(dimethyl siloxane)	0.4
Sulfuric acid	0.05
Isopropyl alcohol	95.55

The solution was prepared using isopropyl alcohol as an organic solvent alcohol well dissolving amino-modified poly(dimethyl siloxane) as the polymer. The amino-modified poly(dimethyl siloxane) used had a structure with one of methyl groups in the repeating unit of poly(dimethyl siloxane) substituted by a functional group having amino group. It was a commercial product (GE Toshiba Silicone, modified

silicone oil TSF47003).

Isopropyl alcohol was first well mixed with amino-modified poly(dimethyl siloxane) added to 0.4 wt.% as polymer concentration in the final solution. Then, sulfuric acid as an inorganic acid was added to the above mixture to 0.05 wt.% as concentrated sulfuric acid concentration in the final solution, and uniformly dissolved therein, to prepare the surface modification solution.

(1) Method for surface treatment of the fibrous absorption body of PP/PE fibers

The absorption body of polypropylene/polyethylene fibers, having the structure shown in FIG. 12A, was immersed in the hydrophobicization-treatment solution 28 of the above composition (FIG. 12B). The solution was held in the voids between the fibrous absorption body. The fibrous absorption body holding the solution was pressed (FIG. 12C), to remove the surplus treatment solution held in the voids between the fibers. When the pressing jig, e.g., metallic mesh, was removed, the fibrous absorption body returned back to the original shape, as shown in FIG. 13A, with the fibers coated with the liquid layer. The absorption body with the fibers wetted with the solution was dried in an oven at 60°C for 1 hour (FIG. 13B).

(Reference Example 3)

The untreated fibrous absorption body of PP/PE fibers was used for Reference Example 3.

Each fibrous absorption body of PP/PE fibers thus prepared was evaluated whether its treated surface conditions were satisfactory or not.

(1) Method for evaluating surface modification of the fibrous absorption body of PP/PE fibers

a) Evaluation by immersion in an aqueous solution of anionic dye

The fibrous absorption bodies of PP/PE fibers, prepared by Example 4 and untreated one (Reference Example 3), were immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as the anionic dye, and then washed with pure water with rubbing, to observe the washed conditions.

b) Results of evaluation of the surface modification of the fibrous absorption body of PP/PE fibers

The following results were obtained by the evaluation tests by immersion in an aqueous solution of anionic dye.

The fibrous absorption body of PP/PE fibers prepared by Example 4 remained lightly cyan in color derived from the dye, when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as the anionic dye, and then washed with pure water with rubbing.

By contrast, the untreated fibrous absorption body

of PP/PE fibers for Reference Example 3 returned back to the original color of white, when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as the anionic dye, and then washed with pure water with rubbing, indicating that the aqueous dye solution was washed off and that it was not compatible with the solution.

As described above, the fibrous absorption body of PP/PE fibers prepared by Example 4, where it was surface-modified with poly(dimethyl siloxane) having amino group as the functional group, remained lightly cyan in color, when immersed in the aqueous dye solution and then washed with water, indicating that the amino-modified poly(dimethyl siloxane) attached to the surfaces of the fibrous absorption body of PP/PE fibers, when the solution containing the amino-modified poly(dimethyl siloxane), acid and alcohol was spread over the surface and dried. In other words, the fibrous absorption body of PP/PE fibers was coated with the amino-modified poly(dimethyl siloxane), and surface-modified into the cationic element by the amino group as a cationic group in the amino-modified poly(dimethyl siloxane). The fibrous absorption body of PP/PE fibers, becoming cationic by the surface modification, reacted with the anionic dye in the aqueous anionic dye solution, to be colored. It was also found that the fibers were colored cyan inside, by

which was indicated that the surface modification method of the present invention effectively modified inside of the fiber assembly of complex structure.

In Example 4, amino-modified poly(dimethyl siloxane) having amino group as a cationic functional group was used for modification of the water-repellent PP surface. However, it is considered that the PP surface can be surface-modified to be anionic, when a functional group other than a cationic one, e.g., anionic functional group, is used as the functional substituent for the poly(dimethyl siloxane) section as the skeleton of amino-modified poly(dimethyl siloxane). An anionic functional group may be used together with an alkali substance as the cleavage catalyst. Thus, it is considered that PP can be surface-modified to have desired properties for specific purposes by changing the functional substituent for the poly(dimethyl siloxane) section as the skeleton to be utilized for the surface deposition, depending on surface modification purposes.

(Example 5)

This example applied the present invention to surface modification of plastic particle surfaces with a solution containing amino-modified poly(dimethyl siloxane). More concretely, the polypropylene particle surfaces were coated, in a manner similar to that for Example 3, with amino-modified poly(dimethyl siloxane)

for surface modification of the water-repellent polypropylene surface.

The hydrophilicization treatment solution having a composition given in Table 5 was prepared.

[Table 5]

(Hydrophilicization treatment solution composition)

Components	Composition (wt.%)
Amino-modified poly(dimethyl siloxane)	0.4
Sulfuric acid	0.05
Isopropyl alcohol	95.55

The solution was prepared by the method similar to that for Example 4. Isopropyl alcohol was first well mixed with amino-modified poly(dimethyl siloxane) added to 0.4 wt.% as polymer concentration in the final solution. Then, sulfuric acid as an inorganic acid was added to the above mixture to 0.05 wt.% as concentrated sulfuric acid concentration in the final solution, and uniformly dissolved therein, to prepare the surface modification solution.

(1) Surface modification of polypropylene (PP) particles

The PP particles used for Example 5 were spherical, having a diameter of 2 mm.

The PP particles were immersed in the above surface modification solution, and then scooped up to be separated from the solution. The PP particles

coated with the treatment solution were put in a container 30 (FIG. 22), and hot wind was vigorously sent into the container, while stirring the particles to prevent fusing these particles with each other, in a manner similar to that for Example 3. These particles were treated during this step by evaporating the solvent and drying the particles.

(Reference Example 4)

The untreated PP particles were used for Reference Example 4.

The treated surface conditions were evaluated by the following methods for the PP particles treated for surface modification (Example 5) and untreated (Reference Example 4).

(1) Method for evaluating surface modification of the PP particles

a) Evaluation by immersion in an aqueous solution of anionic dye

The PP particles, prepared by Example 4 and untreated one (Reference Example 4), were immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as the anionic dye, and then washed with pure water and dried, to observe the washed conditions.

b) Results of evaluation of the surface modification of the PP particles

The following results were obtained by the evaluation tests by immersion in an aqueous solution of

anionic dye.

The PP particles prepared by Example 5 remained lightly cyan in color derived from the dye, when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye as the anionic dye, and then washed with pure water and dried.

By contrast, the untreated PP particles for Reference Example 4 returned back to the original color of white, when immersed in a 10% aqueous solution of C.I. Direct Blue 199 dye, and then washed with pure water and dried, indicating that the aqueous dye solution was washed off and that it was not compatible with the solution.

As described above, the PP particles prepared by Example 5, where it was surface-modified with poly(dimethyl siloxane) having amino group as the functional group, remained lightly cyan in color, when immersed in the aqueous dye solution and then washed with water, indicating that the amino-modified poly(dimethyl siloxane) attached to the surfaces of the PP particles, when the solution containing the amino-modified poly(dimethyl siloxane), acid and alcohol was spread over the surface and dried. In other words, the PP particles were coated with the amino-modified poly(dimethyl siloxane), and surface-modified into the cationic PP particles by the amino group as a cationic group in the amino-modified poly(dimethyl siloxane).

The PP particles, becoming cationic by the surface modification, reacted with the anionic dye in the aqueous anionic dye solution, to be colored.

In the evaluation of the surface modification of the PP particles, cyan dye was used as the anionic dye. However, the PP particles can be colored differently depending on the dye used. This example used the PP particles of 2 mm in diameter. However, use of finer PP particles expands their surface area, possibly improving coloring ratio of the dye on the PP particles and hence producing the brighter particles.

The colored PP particles can be used as the colorant to be dispersed in ink, when they are sufficiently fine.

In Example 5, amino-modified poly(dimethyl siloxane) having amino group as a cationic functional group was used for modification of the water-repellent PP surface. However, it is considered that the PP surface can be surface-modified to be anionic, when a functional group other than a cationic one, e.g., anionic functional group, is used as the functional substituent for the poly(dimethyl siloxane) section as the skeleton of amino-modified poly(dimethyl siloxane). An anionic functional group may be used together with an alkali substance as the cleavage catalyst. Thus, it is considered that PP can be surface-modified to have desired properties for specific purposes by changing

the functional substituent for the poly(dimethyl siloxane) section as the skeleton to be utilized for the surface deposition, depending on surface modification purposes.

(Examples 6 and 7)

Examples 6 and 7 applied the method of the present invention to a fibrous element of PP fibers for hydrophilicization treatment, in addition to Example 2 for the element of PP/PE fibers. More concretely, the element of PP fibers was formed into a rectangular parallelepiped, 2 by 2 by 3 cm in size, comprising the PP fibers of 2 deniers in size.

Two types of the hydrophilicization treatment solution, each having a composition given in Table 5 or 6, were prepared.

[Table 6]

(Hydrophilicization treatment solution composition)

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	0.1
Sulfuric acid	0.0125
Isopropyl alcohol	99.8875

[Table 7]

(Hydrophilicization treatment solution composition)

Components	Composition (wt.%)
Polyoxyalkylene-poly(dimethyl siloxane)	0.1
Sulfuric acid	0.0125
Isopropyl alcohol	40.0
pure water	59.8875

The second composition (for Example 7) was prepared by adding given quantities of isopropyl alcohol and pure water, in this order, to the treatment solution for Example 2, to have the above composition. This solution also contained sulfuric acid and polyoxyalkylene-poly(dimethyl siloxane) diluted 4 times.

The fibrous elements of PP fibers were hydrophilicization-treated, in a manner similar to that for Example 2 for the fibrous element of PP/PE fibers, with the solution of the first composition containing isopropyl alcohol as the major solvent (Example 6) and with the solution of the second composition (Example 7).

(Reference Example 5)

The untreated fibrous element of PP/PE fibers was used for Reference Example 5.

The fibrous element of PP/PE fibers for Reference Example 5, having water-repellent surfaces, was

surface-modified to have hydrophilic surfaces both by Examples 5 and 7, as was the case with the one treated by Example 2. In order to evaluate extent of hydrophilicity, the fibrous elements for Examples 6 and 7 and Reference Example 5 were slowly placed on 7 g of an aqueous ink solution (surface energy: 46 dyn/cm) held by a petri dish.

The untreated fibrous element of PP/PE fibers for Reference Example 5 was observed to float on the aqueous ink. By contrast, those for Examples 5 and 6 absorbed the ink from their bottom surfaces, to clearly different extents, however. The fibrous element for Example 7 totally adsorbed the ink in the petri dish, whereas the one for Example 6 almost the half.

There was no significant difference between quantity of polyoxyalkylene-poly(dimethyl siloxane) coating the fibrous elements for Examples 6 and 7. The difference between these elements in ink-absorbing capacity conceivably resulted from difference in extent of orientation of the polymer itself.

For example, the polymer coating the PE/PP fibrous element for Example 6 was generally oriented, but partially disordered. Orientation of the polymer on the element for Example 7 was disordered to a much smaller extent.

It is considered that the hydrophilicization treatment with polyoxyalkylene-poly(dimethyl siloxane)

gives a denser, better oriented coating layer, when the treatment solution contains a solvent added to water, in addition to isopropyl alcohol. The treatment solution preferably contains at least around 20% of isopropyl alcohol for uniformly wetting the surface. However, the surface may be well coated with a solution containing isopropyl alcohol at below 40% (content of 40% is the level for the solution used in Example 7). Isopropyl alcohol is evaporated faster than other solution components during the solvent evaporation/drying step, decreasing in content faster. When this phenomenon is taken into consideration, the surface can be coated well with a solution containing isopropyl alcohol at below 40%. Moreover, isopropyl alcohol content of below 40% is preferable from industrial safety.

This invention provides an innovative surface modification method capable of performing desired surface modification based on the new mechanism, which uses no ozone, ultraviolet ray or the like for radical formation to process an element for improved properties, nor depends on primer coating (e.g., coating of a silane coupling agent) which may cause uneven coating. This invention also provides a treatment solution for the surface modification method, element produced by the method, and surface structure itself obtained by the surface modification.

In particular, the surface modification method of the present invention tries to give an element surface desired functions and/or characteristics of the surface-modifying polymer by orienting the functional group contained in the polymer at the molecular level. It can effectively modify an element of complex surfaces, e.g., element inner wall surfaces of complex shapes having hollows or voids. Modification by orientation at the molecular level can greatly reduce a required quantity of the modifier. For example, the present invention can uniformly and continuously hydrophilicize surfaces of polyolefin-based resins finding wide use, e.g., polyethylene and polypropylene.